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SCHOOL OF SCIENCE AND TECHNOLOGY

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COURSE TITLE: INDUSTRIAL CHEMICAL TECHNOLOGY I

**COURSE
GUIDE**

**CHM 316
INDUSTRIAL CHEMICAL TECHNOLOGY I**

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INTRODUCTION

You are welcome to this chemistry course. The course will enhance your capacity in the knowledge of industrial development. The knowledge of chemical technology is quite essential and imperative, particularly in the modern era of industrialisation in the world. An effort has been made to cover the necessary outline as prescribed by the National Open University of Nigeria.

The course has been packaged in such a way that you will learn the course using the open learning system techniques available at NOUN. We wish you success in the course and hope you will find it interesting and useful.

WHAT YOU WILL LEARN IN THIS COURSE

The course is entitled “Industrial Chemical Technology 1.” It intends to expose you to the modern practice of chemical operations in the industry. Industrial chemical technology can be described as the scientific background of techniques used in the chemical industries. Therefore, Industrial Chemical Technology 1 will serve as a basis for which the knowledge of transforming raw material into product could be built, as most operation in the industry has to do with heat and mass transfer processes. Also, in this course, you will learn about unit operations which involve most process steps that are described by theories based on conservation of mass, energy and impulse. Lastly, you will also be exposed to the principles and practice of some chemical technology equipment available in the industry.

OBJECTIVES

The important objectives of this course are summarised below. That is, on completion of the course, you should be able to:

- list the day to day problems of chemical technological operations in industries
- discuss heat and mass transfer processes as essential parts of most chemical processes
- analyse the differences between heat and mass transfer operations
- mention some of the various unit operations obtainable in the industry
- identify chemical technology equipment.

COURSE MATERIALS

There are three different sets of course materials that will be used for this course.

- i. A course guide which spells out the broad details of the industrial chemical technology course.
- ii. The study units with detailed learning information. Each study unit has a set of performance objectives along with other relevant learner's guide. Thus, the course is divided into four broad units, each unit having sub-sections.
- iii. A set of recommended chemical process textbooks and relevant websites are listed at the end of each study unit.

STUDY UNITS

Module 1

Unit 1	Heat Transfer Process
Unit 2	Mass Transfer Process
Unit 3	Unit Operations
Unit 4	Chemical Technology Equipment

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MODULE 1

Unit 1	Heat Transfer Process
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UNIT 1 HEAT TRANSFER PROCESS

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1.0 INTRODUCTION

Heat transfer is a discipline that is concerned with the generation, use, conversion, and exchange of thermal energy and heat between physical systems. It is classified into various mechanisms: heat conduction, convection, thermal radiation, and transfer of energy by phase changes. Engineers and industrial technologists also consider the transfer of mass of differing chemical species, either cold or hot, to achieve heat transfer. While these mechanisms have distinct characteristics, they often occur simultaneously in the same system.

Heat conduction, also called diffusion, is the direct microscopic exchange of kinetic energy of particles through the boundary between two systems. When an object is at a different temperature from another body or its surroundings, heat flows so that the body and the surroundings reach the same temperature, at which point they are said to be in a state of thermal equilibrium. Such spontaneous heat transfer occurs from a region of high temperature to another region of lower temperature according to the second law of thermodynamics.

Heat convection occurs when bulk flow of a fluid (gas or liquid) carries heat along with the flow of matter in the fluid. The flow of fluid may be forced by external processes, or sometimes (in gravitational fields) by buoyancy forces caused when thermal energy expands the fluid (for example in a fire plume), thus influencing its own transfer. The latter process is sometimes called "natural convection". All convective processes also move heat partly by diffusion. Another form of convection is forced convection. In this case the fluid is forced to flow by use of a pump, fan or other mechanical means.

The final major form of heat transfer is by radiation, which occurs in any transparent medium (solid or fluid), but may also occur across vacuum (as when the sun heats the earth). Radiation is the transfer of energy through space by means of electromagnetic waves in much the same way as electromagnetic light waves transfer light. The same laws that govern the transfer of light also govern the radiant transfer of heat.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- discuss how heat flows from a higher to lower temperature
- analyse heat exchange in the body
- explain what happens when a body is heated or cooled
- state clearly the laws of thermodynamics.

3.0 MAIN CONTENT

3.1 Heat

Heat is defined as the transfer of thermal energy across a well-defined boundary around a thermodynamic system. It is a characteristic of a process and is not statically contained in matter.

Heat (denoted by the symbol Q) may be seen as something that appears when a system changes its state due to a difference in temperature between the system and its surroundings. Thus, it is a form of energy in transit.

If heat flows into a system from the surroundings, the quantity is said to be positive and conversely, if the heat flows from the system to the surroundings it is said to be negative. In other words:

Heat received or gained by the system = $+Q$

Heat rejected or released or given-out by the system = $-Q$

Heat released by one substance = Heat gained by another substance.

3.2 Definition of Heat Transfer

Heat transfer may be defined as the transmission of energy from one region to another as a result of temperature gradient.

In engineering contexts, however, the term heat transfer has acquired a specific usage, despite its literal redundancy of the characterisation of transfer. In these contexts, heat is taken as synonymous to thermal energy. This usage has its origin in the historical interpretation of heat as a fluid (caloric) that can be transferred by various causes, and that is also common in the language of laymen and everyday life.

Fundamental methods of heat transfer include conduction, convection, and radiation. Physical laws describe the behaviour and characteristics of each of these methods. Real systems often exhibit a complicated combination of all. Heat transfer methods are used in numerous disciplines, such as automotive engineering, thermal management of electronic devices and systems, climate control, insulation, materials processing, and power plant engineering.

Various mathematical methods have been developed to solve or approximate the results of heat transfer in systems. Heat transfer is a path function (or process quantity), as opposed to a state quantity; therefore, the amount of heat transferred in a thermodynamic process that changes the state of a system depends on how that process occurs, not only the net difference between the initial and final states of the process. Heat flux is a quantitative, vectorial representation of the heat flow through a surface.

Heat transfer is typically studied as part of a general chemical engineering or mechanical engineering curriculum. Typically, thermodynamics is a prerequisite for heat transfer courses, as the laws of thermodynamics are essential to the mechanism of heat transfer. Other courses related to heat transfer include energy conversion, thermofluids, and mass transfer.

The transport equations for thermal energy (Fourier's law), mechanical momentum (Newton's law for fluids), and mass transfer (Fick's laws of diffusion) are similar and analogies among these three transport processes have been developed to facilitate prediction of conversion from any one to the others.

3.3 Basic Laws Governing Heat Transfer

- (a) **First Law of Thermodynamics:** This law is based on the law of conservation of energy. It states that energy can be converted from one form to another, but cannot be created or destroyed. Thus, heat lost by one body is equivalent to heat gained by the other body if there is heat transfer process.
- (b) **Second Law of Thermodynamics:** It states that “heat will flow naturally from one reservoir to another at a lower temperature, but not in opposite direction without assistance.”

This law establishes the condition for the direction of energy transport as heat postulates that the flow of energy as heat through a system boundary will always be in direction of lower temperature (or along negative temperature gradient).

- (c) **Third Law of Thermodynamics:** The law can be considered in connection with the determination of entropy to molecular disorder, the greater the disorder or freedom of motions of the atoms or molecules in a system, the greater the entropy of the system. The third law states that “the entropy of a perfect crystalline substance is zero at the absolute zero of temperature.” As the temperature increases, the freedom of motions also increases. Thus, the entropy of any substances above 0K is greater than zero. The importance of the third law of thermodynamics is that it allows us to determine the absolute entropies of substances.

3.4 Modes of Heat Transfer

The fundamental modes of heat transfer are:

- i. Conduction ii. Convection iii. Radiation

3.4.1 Conduction

Conduction is the transfer of heat from one part of a substance to another part of the same substance, or from one substance to another in physical contact with it, without appreciable displacement of molecules forming the substance.

- (a) Thermal Conduction

On a microscopic scale, heat conduction occurs as hot, rapidly moving or vibrating atoms and molecules interact with neighboring atoms and

molecules, transferring some of their energy (heat) to these neighboring particles. In other words, heat is transferred by conduction when adjacent atoms vibrate against one another, or as electrons move from one atom to another. Conduction is the most significant means of heat transfer within a solid or between solid objects in thermal contact. Fluids especially gases are less conductive; the mechanism of heat transfer is simple. The kinetic energy of a molecule is a function of temperature. These molecules are in a continuous random motion exchanging energy and momentum. When a molecule from a higher temperature region collides with a molecule from the low temperature region, it loses energy by collisions. In liquids, the mechanism of heat is nearer to that of gases. However, the molecules are more closely spaced and intermolecular forces come into play.

(b) Steady State Conduction

Steady state conduction (see Fourier's law) is a form of conduction that happens when the temperature difference driving the conduction is constant, so that after an equilibration time, the spatial distribution of temperatures in the conducting object does not change any further. In steady state conduction, the amount of heat entering a section is equal to amount of heat coming out.

(c) Transient Conduction

Transient conduction (see heat equation) occurs when the temperature within an object changes as a function of time. Analysis of transient systems is more complex and often calls for the application of approximation theories or numerical analysis by computer.

Fourier's Law of Heat Conduction

Fourier's Law of heat conduction is an empirical law based on observation and states that 'The rate of flow of heat through a simple homogeneous solid is directly proportional to the area of the section at right angles to the direction of heat flow, and to change of temperature with respect to the length of the path of heat flow'

Mathematically, it can be represented by the equation:

$$\frac{Q}{dx} \propto A \cdot dt$$

Where, Q = Heat flow through a body per unit (in watts), W

A = Surface area of heat flow (perpendicular to the direction of flow) m^2

dt = Temperature difference of the faces of block (homogeneous solid) of thickness

' dx ' through which heat flows, °C or K and

dx = Thickness of body in the direction of flow, m.

Thus,
$$Q = -k \frac{A dt}{dx}$$

Where, k = Constant of proportionality and is known as thermal conductivity of the body.

The -ve sign of k is to take care of the decreasing temperature along with the direction of increasing thickness or the direction of heat flow. The temperature gradient dx/dy is always negative along positive x direction and, therefore, the value Q becomes +ve.

3.4.2 Convection

Convective heat transfer, or convection, is the transfer of heat from one place to another by the movement of fluids, a process that is essentially transferred of heat via mass transfer. The term fluid means any substance that deforms under shear stress; it includes liquids, gases, plasmas, and some plastic solids.) Bulk motion of fluid enhances heat transfer in many physical situations, such as between a solid surface and the fluid. Convection is usually the dominant form of heat transfer in liquids and gases. Although sometimes discussed as a third method of heat transfer, convection is usually used to describe the combined effects of heat conduction within the fluid (diffusion) and heat transference by bulk fluid flow streaming. The process of transport by fluid streaming is known as advection, but pure advection is a term that is generally associated only with mass transport in fluids, such as advection of pebbles in a river. In the case of heat transfer in fluids, where transport by advection in a fluid is always also accompanied by transport via heat diffusion (also known as heat conduction), the process of heat convection is understood to refer to the sum of heat transport by advection and diffusion/conduction.

Free, or natural, convection occurs when bulk fluid motion (streams and currents) are caused by buoyancy forces that result from density variations due to variations of temperature in the fluid. Forced convection is a term used when the streams and currents in the fluid are induced by external means—such as fans, stirrers, and pumps—creating an artificially induced convection current.

Convective heating or cooling in some circumstances may be described by Newton's Law of cooling: "The rate of heat loss of a body is proportional to the difference in temperatures between the body and its

surroundings." However, by definition, the validity of Newton's Law of cooling requires that the rate of heat loss from convection be a linear function of ("proportional to") the temperature difference that drives heat transfer, and in convective cooling this is sometimes not the case. In general, convection is not linearly dependent on temperature gradients, and in some cases is strongly nonlinear. In these cases, Newton's Law does not apply.

3.4.3 Radiation

Thermal radiation

A red-hot iron object transfers heat to the surrounding environment primarily through thermal radiation.

Thermal radiation is energy emitted by matter as electromagnetic waves due to the pool of thermal energy that all matter possesses that has a temperature above absolute zero. Thermal radiation propagates without the presence of matter through the vacuum of space.

Thermal radiation is a direct result of the random movements of atoms and molecules in matter. Since these atoms and molecules are composed of charged particles (protons and electrons), their movement results in the emission of electromagnetic radiation, which carries energy away from the surface.

Unlike conductive and convective forms of heat transfer, thermal radiation can be concentrated in a small spot by using reflecting mirrors, which is exploited in concentrating solar power generation. The properties of radiant heat in general, are similar to those of light. Some of these properties are:

- (i) It does not require the presence of a material medium for its transmission
- (ii) Radiant heat can be reflected from the surfaces and obeys the ordinary laws of reflection
- (iii) It travels with velocity of light
- (iv) Like light, it shows interference, diffraction and polarisation etc.
- (v) It follows the law of inverse square.

The wavelength of heat radiations is longer than that of light waves; hence they are invisible to the eye.

4.0 CONCLUSION

Heat transfer is the common phenomenon in several unit operations such as evaporation, drying and crystallisation, condensation, distillation etc; employed in the transformation of raw materials into products in the industry.

The physical and chemical steps in a process are set with the help of combined knowledge and experience of engineers, industrial chemists, technologists and cost experts to produce a product. The individual operations have some common phenomena and are based on the same scientific principles. For instance, consider two examples of distillation processes which are petroleum distillation and the production of alcoholic beverages. In the first case, oil is separated into its many components, with the lightest at the top and the heaviest on the bottom. In the latter, the gas is enriched in ethanol, which is later re-condensed.

5.0 SUMMARY

You have learnt from this unit that heat is the energy transferred from one body or system to another as a result of a difference in temperature. Heat always migrates from the hotter object to the cooler object, never the other way around. Heat is transferred by three methods: conduction, convection, and radiation. Conduction requires the physical contact of two objects. In the case of a wall, heat is conducted through the layers within the wall from the warmer side to the cooler side. Convection is heat transfer due to fluid or airflow. A common example is when warm air rises (or cool air falls) on a wall's inside surface, inducing air movement. Heat is transferred by radiation when surfaces exchange electromagnetic waves, such as light, infrared radiation, UV radiation or microwaves. Radiation does not require any fluid medium or contact, but does require an air gap or other transparent medium between the surfaces exchanging radiation. Radiation exchange occurs between two surfaces when one is warmer than the other and they are in "view" of each other; i.e., there is nothing between the two surfaces. Also, several laws such as thermodynamics law, Fourier's law of heat conduction, law of cooling were discussed.

6.0 TUTOR-MARKED ASSIGNMENT

- i. Define the following terms: (a) Heat (b) Heat transfer (c) Thermodynamics.
- ii. Enumerate the basic laws which govern heat transfer.
- iii. Name and explain briefly the various modes of heat transfer.
- iv. What is the significance of heat transfer?

- v. How does conduction heat transfer differ from convective heat transfer?
- vi. State Fourier's Law of heat conduction.

7.0 REFERENCES/FURTHER READING

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UNIT 2 MASS TRANSFER PROCESS

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1.0 INTRODUCTION

In unit 1, you learnt about heat transfer as one of the basic operations in the industry and this occurs as a result of temperature gradient. In this unit, you will learn about mass transfer process. Unlike heat transfer which has to do with temperature gradient, mass transfer is as a result of concentration gradient. In a system consisting of one or more components whose concentrations vary from point to point, there is natural tendency for the transport of different species from the region of high to those of low concentrations. Thus, the process of transfer of mass as a result of the species concentration difference in a system/mixture is called mass transfer.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain briefly the term mass transfer
- list the various modes of mass transfer
- state Fick's Law of diffusion
- differentiate between mass concentration and molar concentration
- list several examples of mass transfer operation.

3.0 MAIN CONTENT

3.1 Mass Transfer

Mass transfer is the net movement of mass from one location, usually meaning a stream, phase, fraction or component, to another. Mass transfer occurs in many unit operation processes, such as absorption, evaporation, adsorption, drying, precipitation, membrane filtration, and distillation. Mass transfer is used by different scientific disciplines for different processes and mechanisms. The phrase is commonly used in engineering and applied sciences for physical processes that involve diffusive and convective transport of chemical species within physical systems.

Some common examples of mass transfer processes are the evaporation of water from a pond to the atmosphere, the purification of blood in the kidneys and liver, and the distillation of alcohol. In industrial processes, mass transfer operations include separation of chemical components in distillation columns, absorbents such as scrubbers, adsorbents such as activated carbon beds, and liquid-liquid extraction. Mass transfer is often coupled to additional transport processes, for instance in industrial cooling towers. These towers couple heat transfer to mass transfer by allowing hot water to flow in contact with hotter air and evaporate as it absorbs heat from the air.

3.2 Modes of Mass Transfer

The mechanism of mass transfer depends greatly on the dynamics of the system in which it occurs. Like those of heat transfer, there are different modes of mass transfer. These are:

- (i) Mass transfer by diffusion
- (ii) Mass transfer by convection
- (iii) Mass transfer by change of phase

3.2.1 Mass Transfer by Diffusion (Molecular or Eddy Diffusion)

The transport of water on a microscopic level as a result of diffusion from a region of high concentration to a region of low concentration in a system/mixture of liquids or gases is called molecular diffusion. It occurs when a substance diffuses through a layer of stagnant fluid and may be due to concentration, temperature or pressure gradients. In a gaseous mixture, molecular diffusion occurs due to random motion of the molecules.

When one of the diffusing fluids is in turbulent motion, the eddy diffusion takes place. Mass transfer is more rapid by eddy diffusion than by molecular diffusion. An example of an eddy diffusion process is dissipation of smoke from a smoke stack. Turbulence causes mixing and transfer of smoke to the ambient air.

3.2.2 Mass Transfer by Convection

Mass transfer by convection involves transfer between a moving fluid and a surface, or between two relatively immiscible flowing fluids. The convective mass transfer depends on the transport properties and on the dynamic (laminar or turbulent) characteristics of the flowing fluid. A good example is the evaporation of ether.

3.2.3 Mass Transfer by Change of Phase

Mass transfer occurs whenever a change from one place to another takes place. The mass transfer in such a case occurs due to simultaneous action of convection and diffusion. Some examples are:

- (i) Hot gases escaping from the chimney rise by convection and then diffuse into the air above the chimney.
- (ii) Mixing of water vapour with air during evaporation of water from the lake surface (partly by convection and partly by diffusion).
- (iii) Boiling of water in open air; there is first transfer of mass from liquid to vapour state and then vapour mass from the liquid interface is transferred to the open air by convection as well as diffusion.

3.3 Mass Transfer Operations

When a system contains two or more components whose concentrations vary from point to point, there is a natural tendency for mass to be transferred, minimising the concentration differences within a system.

The transport of one constituent from a region of higher concentration to that of a lower concentration is called mass transfer.

The transfer of mass within a fluid mixture or across a phase boundary is a process that plays a major role in many industrial processes. Examples of such processes are:

- (i) Dispersion of gases from stacks.
- (ii) Removal of pollutants from plant discharge streams by absorption or adsorption.
- (iii) Stripping of gases from waste water.
- (iv) Neutron diffusion within nuclear reactors.
- (v) Air conditioning.
- (vi) Gas absorption.
- (vii) Distillation.
- (viii) Extraction.
- (ix) Adsorption.
- (x) Drying.

Many of day-by-day air experiences also involve mass transfer, for example:

- (i) A lump of sugar added to a cup of coffee eventually dissolves and then eventually diffuses to make the concentration uniform.
- (ii) Water evaporates from ponds to increase the humidity of passing-air-stream.
- (iii) Perfumes present a pleasant fragrance which is imparted throughout the surrounding atmosphere.

3.4 Properties of Mixtures

Mass transfer always involves mixtures. Consequently, we must account for the variation of physical properties which normally exist in a given system. When a system contains three or more components, as many industrial fluid streams do, the problem becomes unwieldy very quickly. The conventional engineering approach to problems of multi-component system is to attempt to reduce them to representative binary (two components) systems.

In order to understand the future discussions, let us first consider definitions and relations which are often used to explain the role of components within a mixture.

3.5 Concentration of Species

Concentration of species in multi-component mixture can be expressed in many ways. For species A, mass concentration denoted by ρ_A is defined as the mass of A, m_A per unit volume of the mixture.

$$\rho_A = \frac{m_A}{V} \quad \text{-----} \quad (1)$$

The total mass concentration density ρ is the sum of the total mass of the mixture in unit volume:

$$\rho = \sum_i \rho_i$$

where ρ_i is the concentration of species i in the mixture.

Molar concentration of, A, C_A is defined as the number of moles of A present per unit volume of the mixture.

By definition,

$$\text{Number of moles} = \frac{\text{mass of A}}{\text{molecular weight of A}}$$

$$n_A = \frac{m_A}{M_A} \quad \text{-----} \quad (2)$$

Therefore from (1) & (2)

$$C_A = \frac{n_A}{V} = \frac{\rho_A}{M_A}$$

For ideal gas mixtures,

$$n_A = \frac{p_A V}{R T} \quad [\text{from Ideal gas law } PV = nRT]$$

$$C_A = \frac{n_A}{V} = \frac{p_A}{R T}$$

where p_A is the partial pressure of species A in the mixture. V is the volume of gas, T is the absolute temperature, and R is the universal gas constant.

The total molar concentration or molar density of the mixture is given by

$$C = \sum_i C_i$$

3.6

Velocities

In a multi-component system the various species will normally move at different velocities; and evaluation of velocity of mixture requires the averaging of the velocities of each species present.

If v_i is the velocity of species i with respect to stationary fixed coordinates, then mass-average velocity for a multi-component mixture defined in terms of mass concentration is,

$$v = \frac{\sum_i \rho_i v_i}{\sum_i \rho_i} = \frac{\sum_i \rho_i v_i}{\rho}$$

Similarly, molar average velocity of the mixture v^* is defined as

$$v^* = \frac{\sum_i C_i v_i}{C}$$

For most engineering problems, there will be little difference in v^* and v and so the mass average velocity, v , will be used in all further discussions.

The velocity of a particular species relative to the mass-average or molar average velocity is termed as diffusion velocity.

Diffusion velocity = $v_i - v$

The mole fraction for liquid and solid mixtures, x_A , and for gaseous mixtures, y_A , are the molar concentration of species A divided by the molar density of the mixtures.

$$x_A = \frac{C_A}{C} \quad (\text{liquids and solids}).$$

$$y_A = \frac{C_A}{C} \quad (\text{gases}).$$

The sum of the mole fractions, by definition must equal 1;

$$\begin{aligned} \text{(i.e.)} \quad \sum_i x_i &= 1 \\ \sum_i y_i &= 1 \end{aligned}$$

Similarly, mass fraction of A in mixture is;

$$w_A = \frac{\rho_A}{\rho}$$

3.7 Diffusion Flux

Just as momentum and energy (heat) transfers have two mechanisms for transport - molecular and convective, so does mass transfer. However, there are convective fluxes in mass transfer, even on a molecular level.

The reason for this is that in mass transfer, whenever there is a driving force, there is always a net movement of the mass of a particular species which results in a bulk motion of molecules. Of course, there can also be convective mass transport due to macroscopic fluid motion.

The mass (or molar) flux of a given species is a vector quantity denoting the amount of the particular species, in either mass or molar units, that passes per given increment of time through a unit area normal to the vector.

3.7.1 Diffusivity

An empirical relation for the diffusional molar flux, first postulated by Fick, often referred to as Fick's first law, defines the diffusion of component A in an isothermal, isobaric system. For diffusion in only the Z-direction, the Fick's rate equation is

$$J_A = -D_{AB} \frac{dC_A}{dZ}$$

where D_{AB} is diffusivity or diffusion coefficient for component A diffusing through component B, and dC_A / dZ is the concentration gradient in the Z-direction.

A more general flux relation which is not restricted to isothermal, isobaric system could be written as

$$J_A = - C D_{AB} \frac{d y_A}{d Z}$$

Fick's Law proportionality, D_{AB} , is known as mass diffusivity (simply as diffusivity) or as the diffusion coefficient. D_{AB} has the dimension of L^2 / t , identical to the fundamental dimensions of the other transport properties: Kinematic viscosity, $\nu = (\mu / \rho)$ in momentum transfer, and thermal diffusivity, $\alpha (= k / \rho C_p)$ in heat transfer.

Diffusivity is normally reported in cm^2 / sec ; the SI unit being m^2 / s or $\text{m}^2 \text{s}^{-1}$.

Diffusivity depends on pressure, temperature, and composition of the system.

In table 1, typical range of values of D_{AB} are given for gas, liquid, and solid systems.

Diffusivities of gases at low density are almost composition independent, while they increase with temperature and vary inversely with pressure. Liquid and solid diffusivities are strongly concentration dependent, while they increase with temperature.

Table 1: General Range of Values of Diffusivity

Type of System	Diffusivities Range ($\text{m}^2 \text{s}^{-1}$)
Gases	$5 \times 10^{-6} - 1 \times 10^{-5}$
Liquids	$10^{-9} - 10^{-6}$
Solids	$5 \times 10^{-14} - 1 \times 10^{-10}$

In the absence of experimental data, semi-theoretical expressions have been developed which give approximation, sometimes as valid as experimental values, due to the difficulties encountered in experimental measurements.

3.7.2 Diffusivity in Gases

Pressure dependence of diffusivity is given by

$$D_{AB} \propto \frac{1}{P} \quad \text{--(for moderate ranges of pressures, up to 25 atm).}$$

And temperature dependency is according to

$$D_{AB} \propto T^{3/2}$$

Diffusivity of a component in a mixture of components can be calculated using the diffusivities for the various binary pairs involved in the mixture. The relation given by Wilke is

$$D_{1\text{-mixture}} = \frac{1}{\frac{y_2}{D_{1-2}} + \frac{y_3}{D_{1-3}} + \dots + \frac{y_n}{D_{1-n}}}$$

Where $D_{1\text{-mixture}}$ is the diffusivity for component 1 in the gas mixture; D_{1-n} is the diffusivity for the binary pair, component 1 diffusing through component n; and y_n' is the mole fraction of component n in the gas mixture evaluated on a component 1 – free basis, that is

$$y_2' = \frac{y_2}{y_2 + y_3 + \dots + y_n}$$

3.7.3 Diffusivity in Liquids

Diffusivity in liquid is exemplified by the values given in table 1. Most of these values are nearer to $10^{-5} \text{ cm}^2 / \text{sec}$, and about ten thousand times lower than those in dilute gases. This characteristic of liquid diffusion often limits the overall rate of processes accruing in liquids (such as reaction between two components in liquids).

In chemistry, diffusivity limits the rate of acid-base reactions; in the chemical industry, diffusion is responsible for the rates of liquid-liquid extraction. Diffusion in liquids is important because it is slow.

Certain molecules diffuse as molecules, while others which are designated as electrolytes ionise in solutions and diffuse as ions. For example, sodium chloride (NaCl), diffuses in water as Na^+ and Cl^- ions. Though each ion has a different mobility, the electrical neutrality of the

solution indicates the ions must diffuse at the same rate; accordingly, it is possible to speak of a diffusion coefficient for molecular electrolytes such as NaCl. However, if several ions are present, the diffusion rates of the individual cations and anions must be considered, and molecular diffusion coefficients have no meaning.

Diffusivity varies inversely with viscosity when the ratio of solute to solvent ratio exceeds five. In extremely high viscosity materials, diffusion becomes independent of viscosity.

3.7.4 Diffusivity in Solids

Typical values for diffusivity in solids are shown in table 1. One outstanding characteristic of these values is their small size, usually thousands of times less than those in a liquid, which are in turn 10,000 times less than those in a gas.

Diffusion plays a major role in catalysis and is important to the chemical engineer and industrial chemist. For metallurgists, diffusion of atoms within the solids is of more importance.

3.7.5 Diffusion in Solids

In certain units operations of chemical engineering such as in drying or in absorption, mass transfer takes place between a solid and a fluid phase. If the transferred species is distributed uniformly in the solid phase and forms a homogeneous medium, the diffusion of the species in the solid phase is said to be structure-independent. In this case diffusivity or diffusion coefficient is direction – independent. At steady state, and for mass diffusion which is independent of the solid matrix structure, the molar flux in the z direction according to Fick's Law is given by:

$$N_A = -D_{AB} \frac{dC_A}{dz} = \text{constant},$$

Integrating the above equation,

$$N_A = \frac{D}{z} \frac{(C_1 - C_2)}{AB}$$

which is similar to the expression obtained for diffusion in a stagnant fluid with no bulk motion (i.e. $N = 0$).

Example: A steel rectangular container having walls 16mm thick is used to store hydrogen gas at elevated pressure. The molar concentrations of hydrogen in the steel at the inside and outside surfaces are 1.2kg mole/m³ and zero respectively. Assuming the diffusion

coefficient for hydrogen in steel as $0.248 \times 10^{-12} \text{ m}^2/\text{s}$, Calculate the molar diffusion flux for hydrogen through the steel.

Solution: Given $Z = 16 \text{ mm} = 0.016 \text{ m}$, $C_{A1} = 1.2 \text{ kg mole/m}^3$, $C_{A2} = 0$, $D_A = 0.248 \times 10^{-12} \text{ m}^2/\text{s}$

Assuming one dimensional and steady state condition, the molar diffusion flux rate in the steel is given by Fick's law of diffusion

$$\begin{aligned} \text{Molar diffusion Flux } N_A &= \frac{D}{Z} (C_1 - C_2) \\ &= \frac{0.248 \times 10^{-12}}{0.016} (1.2 - 0) \end{aligned}$$

=18.6

**x 10⁻¹²
12kg mole/s.m²**

3.7.6 Diffusion in Process Solids

In some chemical operations, such as heterogeneous catalysis, an important factor, affecting the rate of reaction is the diffusion of the gaseous component through a porous solid. The effective diffusivity in the solid is reduced below what it could be in a free fluid, for two reasons. First, the tortuous nature of the path increases the distance, which a molecule must travel to advance a given distance in the solid. Second, the free cross-sectional area is restricted. For many catalyst pellets, the effective diffusivity of a gaseous component is of the order of one tenth of its value in a free gas.

If the pressure is low enough and the pores are small enough, the gas molecules will collide with the walls more frequently than with each other. This is known as Knudsen flow or Knudsen diffusion. Upon hitting the wall, the molecules are momentarily absorbed and then given off in random directions. The gas flux is reduced by the wall collisions. By the use of the kinetic flux, the concentration gradient is independent of pressure; whereas the proportionality constant for molecular diffusion in gases (diffusivity) is inversely proportional to pressure.

Knudsen diffusion occurs when the size of the pore is of the order of the mean free path of the diffusing molecule.

3.7.7 Transient Diffusion

Transient processes, in which the concentration at a given point varies with time, are referred to as unsteady state processes or time-dependent processes. This variation in concentration is associated with a variation in the mass flux.

These generally fall into two categories:

- i) The process which is in an unsteady state only during its initial startup.
- ii) The process which is in a batch operation throughout its operation.

In unsteady state processes, there are three variables - concentration, time and position. Therefore the diffusion process must be described by partial rather than ordinary differential equations.

Although the differential equations for unsteady state diffusion are easy to establish, most solutions to these equations have been limited to situations involving simple geometries and boundary conditions, and a constant diffusion coefficient.

Many solutions are for one-directional mass transfer as defined by Fick's second law of diffusion:

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial z^2}$$

This partial differential equation describes a physical situation in which there is no bulk-motion contribution, and there is no chemical reaction. This situation is encountered when the diffusion takes place in solids, in stationary liquids, or in system having equimolar counter diffusion. Due to the extremely slow rate of diffusion within liquids, the bulk motion contribution of flux equation (i.e., $y_A \sum N_i$) approaches the value of zero for dilute solutions; accordingly this system also satisfies Fick's second law of diffusion.

The solution to Fick's second law usually has one of the two standard forms. It may appear in the form of a trigonometric series which converges for large values of time, or it may involve series of error functions or related integrals which are most suitable for numerical evaluation at small values of time. These solutions are commonly obtained by using the mathematical techniques of separation of variables or Laplace transforms.

4.0 CONCLUSION

Mass transfer phenomena can now be observed in many fields of industry. In particular, separation processes, which make up the vast majority of industrial production procedures, are governed by the physics of mass transfer, and their design and optimisation depend

heavily on knowledge in this field. Gas absorption, distillation, extraction, adsorption, drying are all parts of mass transfer processes.

5.0 SUMMARY

In this unit, you have learnt that mass transfer is the net movement of mass from one location, usually meaning a stream, phase, fraction or component, to another and, the process of transfer of mass is as a result of the species concentration difference in a system/mixture. In industrial processes, mass transfer operations include separation of chemical components in distillation columns, absorbents such as scrubbers, adsorbents such as activated carbon beds, and liquid-liquid extraction.

Mass transfer occurs in many unit operation processes, such as absorption, evaporation, adsorption, drying, precipitation, membrane filtration, and distillation. Also, other modes of mass transfer are diffusion, convection and change of phase. Mass transfer always involves mixtures. Consequently, concentration, diffusivity in gases, liquids and solids were equally discussed. An empirical relation for the diffusional molar flux, first postulated by Fick and, accordingly, often referred to as Fick's first law is also mentioned.

6.0 TUTOR-MARKED ASSIGNMENT

- i. Explain briefly the term mass transfer.
- ii. Enumerate application of mass transfer.
- iii. List the various modes of mass transfer.
- iv. State Fick's law of diffusion.
- v. Define molar concentration.

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UNIT 3 UNIT OPERATIONS

CONTENTS

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1.0 INTRODUCTION

Every industrial chemical process is based on unit operations (physical treatment) and unit process (chemical treatment) to produce economically desired product from specific raw materials. The raw materials are treated through physical steps to make them suitable for chemical reaction. So, knowledge of unit operations like 'mixing and agitation of liquid' and 'heat flow' is very much necessary. The subject Unit Operations is based on fundamental laws and physicochemical principles. Unit operation gives idea about science related to specific physical operation; different equipments-its design, material of construction and operation; and calculation of various physical parameters (mass flow, heat flow, mass balance, power and force etc.). Examples of unit operations are: heat flow, fluid flow, mixing, drying, absorption, evaporation, adsorption, distillation, condensation, crystallisation, vapourisation, leaching, separation, extraction, sedimentation, filtration, crushing e.tc.

2.0 OBJECTIVES

At end of this unit, you should be able to:

- define a unit operation and unit process
- differentiate between unit operation and unit process
- list some examples of unit operation.

3.0 MAIN CONTENT

3.1 Unit Operation

A unit operation is any part of potentially multiple-step process which can be considered to have a single function. It is a basic step in a process. Unit operations involve bringing a physical change such as separation, crystallisation, evaporation, filtration etc. For example, in milk processing: homogenisation, pasteurisation, chilling, and packaging are individual unit operations which are connected to create the overall process. A process may have many unit operations to obtain the desired product.

Historically, the different chemical industries were regarded as different industrial processes and with different principles. Arthur Dehon Little (1916) propounded the concept of "Unit Operations" to explain industrial chemistry processes., William H.Walker, Warren K. Lewis and William H. McAdams (1923), explained that variety of chemical industries have processes which follow the same physical laws. They summed-up these similar processes into unit operations. Each unit operation follows the same physical laws and may be used in all chemical industries. The unit operations form the fundamental principles of chemical technology.

After preparing raw materials by physical treatment, these undergo chemical conversion in a reactor. To perform chemical conversion basic knowledge of stoichiometry, reaction kinetics, thermodynamics, chemical equilibrium, energy balance and mass balance is necessary. Many alternatives may be proposed to design a reactor for a chemical process. One design may have low reactor cost, but the final materials leaving the unit need higher treatment cost while separating and purifying the desired product. Therefore, the economics of the overall process also play a vital role to select a suitable alternative design. Each chemical process consists of series of assembly that are organised systematically to achieve the goal. The physical and chemical steps in a process are set with the help of combined knowledge and experience of engineers, industrial chemists, technologists and economists to produce a product. The individual operations have some common phenomena and are based on the same scientific principles e.g. heat transfer is the common phenomenon in evaporation, drying and crystallisation.

A process designer designs a chemical process based on the following:

- (1) Efficiency of process and equipments
- (2) Safety with respect to the process, raw chemicals, finished products and long term effect on environment

(3) Financial viability of the products as demanded by the purchaser.

The following are some examples of physical processes:

(a) Sugar Manufacture:

Sugar cane → crushing → sugar extraction → thickening of syrup → evaporation of water → sugar crystallization → filtration → drying → screening → packaging.

(b) Pharmaceutical Manufacture:

Formulation of chemicals, mixing, granulation → drying of granules → screening → pressing tablet → packaging.

(c) Salt Manufacture:

Brine transportation → evaporation → crystallization → drying → screening → conveying → packaging.

On the other hand conversion of starch to dextrose with the help of acid catalyst is a typical chemical reaction which involves transportation of raw materials, physical steps of mixing the reactants, heat transfer, reaction kinetics, fluid flow, separation of products, product purification, drying, screening, conveying and packaging.

In pharmaceutical curriculum, knowledge of unit operations is very much relevant particularly with respect to **formulated drug products** and **basic drugs**.

3.2 Unit Process

A unit process is a step in manufacturing in which chemical reaction takes place, e.g. the oxidation of paraxylene to terephthalic acid is a unit process, the hydrogenation of vegetable oil to ghee is a unit process. Others include, nitration, sulphonation, hydroformylation e.t.c.

Unit operations and unit processing form the main principles of all kinds of chemical industries and are the foundation of designs of chemical plants, factories, and equipment used.

3.3 Industrial Processes

Large processes are broken into unit operations in order to make them easier to analyse. The key thing to remember about them is that the conservation laws apply not only to the process as a whole but also to

each individual unit operation. Examples of such processes are discussed below.

3.3.1 Mixing

Mixing can be termed as the preparation of mixture of substances either in solids, liquids, or gaseous form. It is an essential part of most production processes in chemical and allied industries covering all processing stages from the preparation of reagents to the final blending of products. The equipment used depends on the nature of the materials and the degree of mixing required. Mixing process can be considered under three stages.

- (a) **Gas Mixing:** Specialised equipment is seldom needed for mixing gases, which mix easily because of their low viscosities. The mixing given by turbulent flow in a length of pipe is usually sufficient for most purposes. Turbulent promoters, such as orifices or baffles can be used to increase the rate of mixing. In most cases, in-line mixers are always used.
- b) **Liquid Mixing:** The following factors must be taken into account when choosing equipment for mixing liquids:
 - (i) Batch or continuous operation.
 - (ii) Nature of the process whether is miscible or immiscible liquids or dispersion liquid.
 - (iii) Degree of mixing required.
 - (iv) Physical properties of the liquid, particularly the viscosity.
 - (v) Whether the mixing is associated with other operations such as reaction, heat transfer e.t.c.
- (c) **Solids and Pastes:** Mixing of solid is carried out by using various types of highly specialised equipment. Such equipment include cone blenders which are used for free flowing solids, ribbon blender for dry solid and for blending liquids with solid while Z- blade mixers and pan mixers are used for kneading heavy pastes and dough.

3.3.2 Agitation

Agitation refers to the induced motion of a material in a specified way, usually in a circulatory pattern inside some sort of container. Agitation involves both homogeneous and heterogeneous phases while mixing is used for heterogeneous phase. For example, water in a cup can be agitated but cannot be referred to as mixed. Thus, agitation is not the same as mixing.

3.4 Separation Processes

There are different types of separation processes. These include: distillation, extraction, absorption, membrane filtration, and so on. Each of these can also be used for purification, to varying degrees.

(a) Separation by Flashing

A mixture of two liquids or a liquid and vapour can be separated by passing it to a flash drum at a fixed temperature and pressure. The mixture is allowed to reach equilibrium (or near it), and then the vapour exits the top and the liquid exits the bottom of the drum. This separates the components somewhat, provided that the temperature is chosen between the boiling temperatures of the components of the mixture at the pressure of the drum. The degree of separation depends on the composition of the mixture, the concentrations of the species in the mixture, and the temperature and pressure. Having data such as fugacity data or even vapour pressures for simple modeling like Raoult's Law are invaluable when choosing the operating conditions.

When a solution boils, the resulting gas is still a mixture, but the gaseous mixture will in general have more of the lower-boiling compound than the higher-boiling compound. Therefore, a higher-boiling compound can be separated from the lower-boiling compound by simply allowing a part of the solution to boil and another part to remain as liquid.

(b) Distillation

Distillation is the most widely used separation process in the chemical industry. It is also known as fractional distillation or fractionation. It is normally used to separate liquid mixtures into two or more vapour or liquid products with different compositions.

Distillation is an equilibrium stage operation. In each stage, a vapour phase is contacted with a liquid phase and mass is from vapour to liquid and from liquid to vapour. The less volatile, heavy or high-boiling components concentrate in the liquid phase; the more volatile, light components concentrate in the vapour. By using multiple stages in series with recycle, separation can be accomplished.

Operating Principles

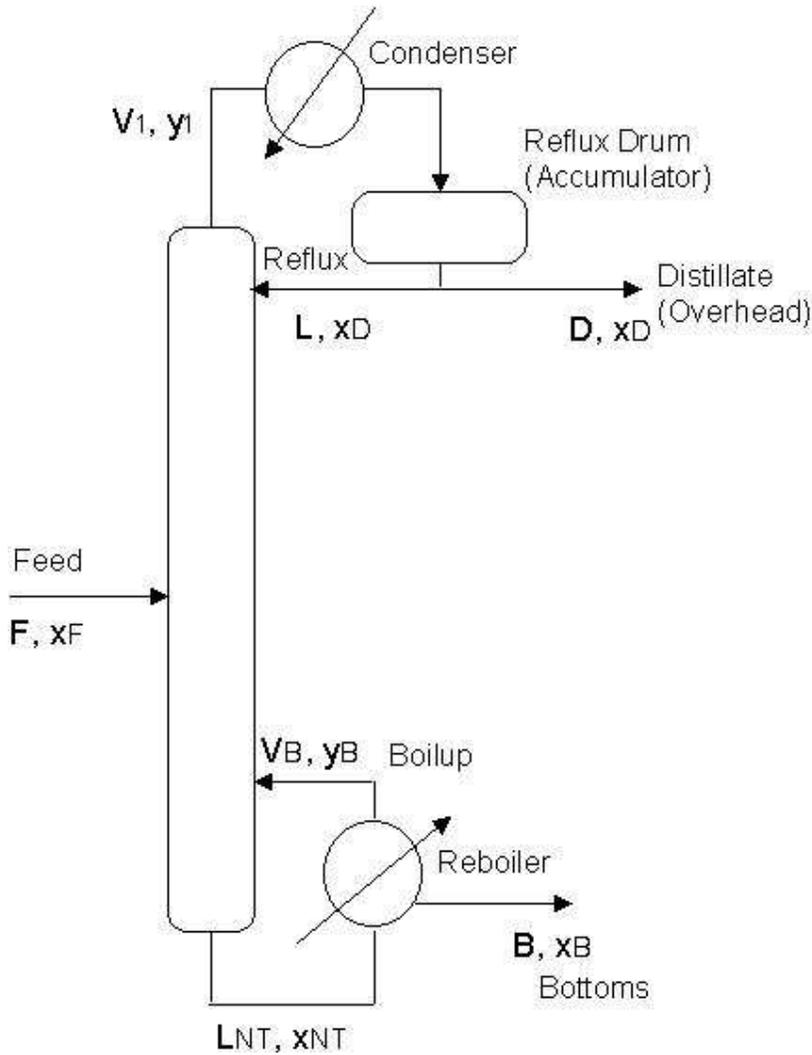


Fig.1: Schematic Representation of the Operating Principles of Distillation

The feed to a distillation column may be liquid, vapour, or a liquid-vapour mixture. It may enter at any point in the column, although the optimal feed tray location should be determined and used. More than one stream may be fed to the system, and more than one product may be drawn.

A column is divided into series of stages. These correspond to a cascade of equilibrium stages. Liquid flows down the column from stage to stage and is contacted by vapour flowing upward.

Traditionally, most columns have been built from a set of distinct trays or plates, so these terms end up being essentially interchangeable with

stages. Each tray in a distillation column is designed to promote contact between the vapour and liquid on the stage. Distillation can be conducted in a packed column (just as absorption can be done in a trayed column), but we will focus on trayed columns for the present. A schematic illustration of the operating principles of distillation is shown in Fig.1.

The product leaving the top of the column is called the overhead product, the overhead, the top product, the distillate, or distillate product. Distillate product may be liquid or vapour (or occasionally both) depending on the type of condenser used. Most of the time the distillate flow rate is assigned the symbol D , and the composition x_D or y_D .

The product leaving the bottom of the column is called the bottom product or bottoms, and given the symbol B , with composition x_B .

In some situations, notably petroleum refining, one or more intermediate or "sidedraw" products may be removed from the column.

Vapour leaving the top of the column passes through a heat exchanger, the condenser, where it is partially or totally condensed. The liquid which results is temporarily held in the accumulator or reflux drum. A liquid stream is withdrawn from the drum and returned to the top tray of the column as reflux (R or L) to promote separation.

The portion of the column above the feed tray is called the rectification section. In this section, the vapour is enriched by contact with the reflux. The portion of the column below the feed tray is called the stripping section. The liquid portion of the feed serves as the reflux for this section.

The operating pressure of the column is typically controlled by adjusting heat removal in the condenser.

The base of the column is typically used as a reservoir to hold liquid leaving the bottom tray. A heat exchanger, the re-boiler, is used to boil this liquid. The vapour which results, the boil-up (V) is returned to the column on one of the bottom three or four trays.

In normal operation, there are five handles that can be adjusted to manipulate the behaviour of a distillation column – the feed flow, two product flows, the reflux flow, and the boil-up flow (or re-boiler heat input).

A normal column has a temperature gradient and a pressure gradient from bottom to top.

Distillation, like flashing, is a process which is generally used to separate a mixture of two or more liquids based on their boiling points. However, what happens in a distillation column is essentially a series of flashes, which are connected with recycle loops. The liquid from each tray comes to equilibrium (ideally) with the vapour, and the vapour rises up to the next tray and the liquid falls to the tray beneath it. Each tray has a different temperature because a re-boiler on the bottom and a condenser at the top maintain a temperature gradient across the column (in certain separation setups one of these components is omitted).

The net result is, like flashing, more of the lower-boiling compound(s) will exit at the top of the column, and more of the higher-boiling compound(s) will fall to the bottoms. Since distillation is multiple flashes in a row, it is typically more effective than a single flash, although the latter may be sufficient depending on the purpose. Distillation columns are standard for many types of separations because it is relatively inexpensive for its efficacy. Distillation has a limit, however; non-ideal mixtures can form azeotropes. An azeotrope is a point at which when the solution boils, the vapour has the same composition as the liquid. Therefore no further separation can be done without another method or without using some special tricks.

Two examples of distillation processes are petroleum distillation and the production of alcoholic beverages. In the first case, oil is separated into its many components, with the lightest at the top and the heaviest on the bottom. In the latter, the gas is enriched in ethanol, which is later recondensed.

(c) Gravitational Separation

Gravitational separation takes advantage of the well-known effect of density differences. Something that is less dense will float on something that is denser. Therefore, if two immiscible liquids have significantly different densities, they can be separated by simply letting them settle, then draining the denser liquid out via the bottom. Note that the key word here is immiscible; if the liquids are soluble in each other, then it is impossible to separate them by this method.

This method can also be used to separate out solids from a liquid mixture, but again the solids must not be soluble in the liquid (or must be less soluble than they are as present in the solution).

(d) Extraction

Extraction is the general practice of taking something liquid and forcing it to become dissolved in another liquid. This is done by taking advantage of the **relative solubility** of a compound between two liquids. For example, caffeine must be extracted from coffee beans or tea leaves in order to be used in beverages such as coffee or soda. The common method for doing this is to use CO_2 which is able to dissolve caffeine as if it were a liquid. Then, in order to take the caffeine out, the temperature is lowered (lowering in carbon dioxide) and water is injected. The system is then allowed to reach equilibrium. Since caffeine is more soluble in water than it is in carbon dioxide, the majority of it goes into the water.

Extraction is also used for purification. If a stream is contaminated with a pollutant, the pollutant can be extracted with another, clean stream. Even if it is not very soluble, it will still extract pollutant.

Another type of extraction is acid-base extraction, which is useful for moving a basic or acidic compound from a polar solvent (such as water) to a non-polar one. Often, the ionised form of the acid or base is soluble in a polar solvent, but the non-ionised form is more soluble in a non-polar solvent. To manipulate where the majority of the compound will end up, we alter or adjust the pH of the solution by adding acid or base.

For example, suppose you wanted to extract fluoride (F^-) from water into benzene. First, you would add acid, because when a strong acid is added to the solution it undergoes the following reaction with fluoride, which is practically irreversible:



The hydrogen fluoride is more soluble in benzene than fluoride itself, so it would move into the benzene. The two solutions could then be separated by density since they are immiscible. The term **absorption** is a generalisation of extraction that can involve different phases (gas-liquid instead of liquid-liquid). However, the ideas are still the same.

(e) Membrane Filtration

A membrane is any barrier which allows one substance to pass through it more than another. There are two general types of membrane

separators: those which separate based on the size of the molecules and those which separate based on diffusivity.

An example of the first type of membrane separator is your everyday vacuum cleaner. Vacuum cleaners work by taking in air laden with dust from your carpet. A filter inside the vacuum then traps the dust particles (which are relatively large) and allows the air to pass through it (since air particles are relatively small). A larger-scale operation that works on the same principle is called a **fabric filter** or "Baghouse", which is used in air pollution control or other applications where a solid must be removed from a gas.

Some fancy membranes exist which are able to separate hydrogen from a gaseous mixture by size. These membranes have very small pores which allow hydrogen (the smallest possible molecule, by molecular weight) to pass through by convection, but other molecules cannot pass through the pores and must resort to diffusion (which is comparatively slow). Hence a purified hydrogen mixture results on the other side.

Membranes can separate substances by their diffusivity as well, for example water may diffuse through a certain type of filter faster than ethanol, so if such a filter existed it could be used to enrich the original solution with ethanol.

3.5 Purification Methods

In order to bring any product to market, it is necessary to purify it adequately. Without purification, people could get sick from eating such foods; side effects could occur in industry which would cause safety concerns, or a scientist's research could be invalidated. Fortunately there are several methods that are commonly used for purification. The separation processes mentioned above are often used for this purpose, as are the following two processes.

(a) Adsorption

This should not be confused with absorption; adsorption is a process which separates components by their relative adhesiveness to a surface. An adsorption column is essentially a pipe filled with a certain material. When the contaminant flows by, it will bind to the material, and in this way the fluid flowing by is cleaned. Adsorption is therefore a surface phenomenon.

A major disadvantage to this method is that the material will always have a *saturation point* after which no more contaminant can latch on to

it. At this point, the process of purification stops and therefore the spent material must be replaced by new material.

(b) Re-Crystallisation

Re-crystallisation is the purification of substances by taking advantage of changes in solubility with respect to temperature. We take advantage of this by dissolving an impure compound and then lowering the temperature slowly. The solubility of most solid substances increases with temperature, so decreasing the temperature will cause the solubility of both the impurities and the substance to be purified to decrease. However, since there is likely much more of the impure substance present than impurities, the impure substance will eventually crystallise out long before the impurities. Therefore, as long as the temperature is not lowered too quickly, the impure substances will crystallise out in a purer form, while most impurities will remain in solution. A disadvantage to this method is that it takes a long time to perform, but it is often the most effective method for obtaining a pure sample of a product.

4.0 CONCLUSION

Most unit operations are based mechanically upon the fundamental transport processes of mass transfer, heat transfer, and fluid flow (momentum transfer). Unit operations based on fluid mechanics include fluid transport (such as pumping), mixing/agitation, filtration, clarification, thickening or sedimentation, classification, and centrifugation. Operations based on heat transfer include heat exchange, condensation, evaporation, furnaces or kilns, drying, cooling towers, and freezing or thawing. Operations that are based on mass transfer include distillation, solvent extraction, leaching, absorption or desorption, adsorption, ion exchange, humidification or dehumidification, gaseous diffusion, crystallisation, and thermal diffusion. Operations that are based on mechanical principles include screening, solids handling, size reduction, flotation, magnetic separation, and electrostatic precipitation. The study of transport phenomena provides a unifying and powerful basis for an understanding of the different unit operations.

5.0 SUMMARY

You have learnt from this unit that every industrial chemical process is based on unit operations (physical treatment) such as mixing, drying, absorption, evaporation, adsorption, distillation, condensation, crystallization, vaporization, leaching, separation, extraction, sedimentation, filtration, crushing as well as unit processes (chemical treatment) such as oxidation, hydrogenation, alkylation, polymerisation,

nitration etc; produce economically a desired product from specific raw materials. The raw materials are treated through physical steps to make it suitable for chemical reaction. So, knowledge of unit operations like mixing and agitation of liquid and heat flow is very much necessary.

6.0 TUTOR-MARKED ASSIGNMENT

- i. What is unit operation?
- ii. Differentiate between unit operation and unit process.
- iii. List examples of industrial processes.
- iv. What is distillation?
- v. Differentiate between adsorption and absorption.
- vi. Give several examples of unit operation.

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UNIT 4 CHEMICAL TECHNOLOGY EQUIPMENT

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 - 3.2 Chemical Technology Equipment
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1.0 INTRODUCTION

In units 1 and 2, heat and mass transfer were discussed in relation to industrial chemical technology respectively. In unit 3, various unit operations were discussed and it is specifically stated that every industrial chemical process is based on unit operations (physical treatment) and unit process (chemical treatment) to produce economically a desired product from specific raw materials. The raw materials are treated through physical steps to make them suitable for chemical reaction and this involved the use of different types of equipment for the objectives to be realised. In this unit, some of the equipment available in carrying out such unit operations will be discussed.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- list some chemical technology equipment available for industrial development
- state the relevance of this equipment to the industry.

3.0 MAIN CONTENT

3.1 Chemical Technology

Chemical technology can be described as the scientific techniques used in the chemical industry. It is the science of those operations which convert raw materials into desired products on an industrial scale, applying one or more chemical conversions. The route along which a raw material is converted to products is a logical coupling of interconnected operations terms industrial processes which involve unit operation and unit process (see unit 3).

3.2 Chemical Technology Equipment

These are equipments used in facilitating or involved in the transformation of raw materials into products. The equipment helps in transfer of heat and mass from one point to another in order to achieve production processes. The first steps in a process, such as the mechanical operations of grinding or crushing, are often followed by physical treatments such as mixing, heating, evaporating, distilling, condensing e.t.c. are carried out via chemical technology equipment. Some of these equipments are discussed below.

3.2.1 Heat Exchangers

In general, a heat exchanger is a device which is used to facilitate the exchange of heat between two mixtures, from the hotter one to the cooler one. It is any equipment which transfers the energy from a hot fluid to a cold fluid, with maximum rate and minimum investment and running costs. Heat exchangers very often involve steam because steam is very good at carrying heat by convection, and it also has a high heat capacity so it will not change temperature as much as another working fluid would. In addition, though steam can be expensive to produce, it is likely to be relatively less expensive compare to other working fluids since it comes from water. Examples of heat exchangers are:

- i) Intercooler and pre-heater
- ii) Condenser and boilers in steam plant
- iii) Condensers and evaporators in refrigeration units
- iv) Regenerators
- v) Radiators
- vi) Oil coolers e.t.c.

Tubular Heat Exchangers

A tubular heat exchanger is essentially a jacket around a pipe. The working fluid (often steam) enters the jacket on one side of the heat exchanger and leaves on the other side. Inside the pipe is the mixture which you want to heat or cool. Heat is exchanged through the walls of the device in accordance to the second law of thermodynamics, which requires that heat flow from higher to lower temperatures. Therefore, if it is desired to cool off the fluid in the pipe, the working fluid must be cooler than the fluid in the pipe.

Tubular heat exchangers can be set up in two ways: co-current or counter-current. In a co-current setup, the working fluid and the fluid in the pipe enter on the same side of the heat exchanger. This setup is somewhat inefficient because as heat is exchanged, the temperature of the working fluid will approach that of the fluid in the pipe. The closer the two temperatures become, the less heat can be exchanged. Worse, if the temperatures become equal somewhere in the middle of the heat exchanger, the remaining length is wasted because the two fluids are at thermal equilibrium (no heat is released).

To help counteract these effects, one can use a counter-current setup, in which the working fluid enters the heat exchanger on one end and the fluid in the pipe enters at the other end. As an explanation for why this is more efficient, suppose that the working fluid is hotter than the fluid in the pipe, so that the fluid in the pipe is heated up. The fluid in the pipe will be at its highest temperature when it exits the heat exchanger and at its coolest when it enters. The working fluid will follow the same trend because it cools off as it travels the length of the exchanger. Because it's counter-current, though, the fact that the working fluid cools off has less of an effect because it's exchanging heat with cooler, rather than warmer, fluids in the pipe.

3.2.2 Distillation Towers

Large scale industrial distillation applications include both batch and continuous fractional, vacuum, azeotropic, extractive, and steam distillation. The most widely used industrial applications of continuous, steady-state fractional distillation are in petroleum refineries, petrochemical and chemical plants and natural gas processing plants. Industrial distillation is typically performed in large, vertical cylindrical columns known as **distillation towers** or **distillation columns** with diameters ranging from about 65 centimetres to 16 metres and heights ranging from about 6 to 90 metres or more. When the process feed has a diverse composition, as in distilling crude oil, liquid outlets at intervals up the column allow for the withdrawal of different fractions or products

having different boiling points or boiling ranges. The lightest products (those with the lowest boiling point) exit from the top of the columns and the heaviest products (those with the highest boiling point) exit from the bottom of the column and are often called the bottoms. A typical industrial distillation tower diagram is shown in Fig. 2.

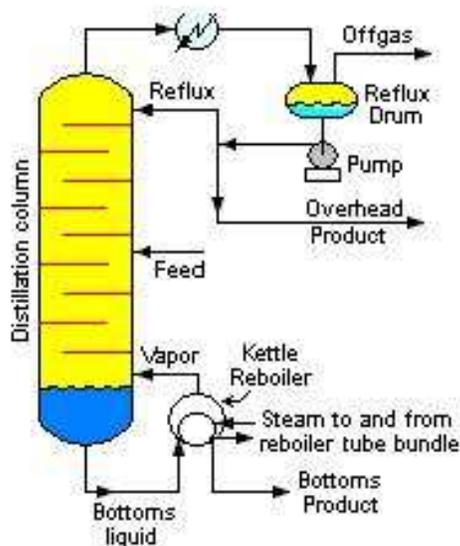


Fig.2: Diagram of a Typical Industrial Distillation Tower

Industrial towers use reflux to achieve a more complete separation of products. Reflux refers to the portion of the condensed overhead liquid product from a distillation or fractionation tower that is returned to the upper part of the tower as shown in the schematic diagram of a typical, large-scale industrial distillation tower. Inside the tower, the down flowing reflux liquid provides cooling and condensation of the up flowing vapours thereby increasing the efficiency of the distillation tower. The more reflux that are provided for a given number of theoretical plates, the better the tower's separation of lower boiling materials from higher boiling materials. Alternatively, the more reflux that is provided for a given desired separation, the fewer the number of theoretical plates required.

Such industrial fractionating towers are also used in air separation, producing liquid oxygen, liquid nitrogen, and high purity argon. Distillation of chlorosilanes also enables the production of high-purity silicon for use as a semiconductor.

The efficiencies of the vapour-liquid contact devices (referred to as plates or trays) used in distillation towers are typically lower than that of a theoretical 100% efficient equilibrium stage. Hence, a distillation tower needs more trays than the number of theoretical vapor-liquid equilibrium stages.

In modern industrial uses, generally, a packing material is used in the column instead of trays, especially when low pressure drops across the column are required, as when operating under vacuum.

This packing material can either be random dumped packing (1-3" wide) such as Raschig rings or structured sheet metal. Liquids tend to wet the surface of the packing and the vapours pass across this wetted surface, where mass transfer takes place. Unlike conventional tray distillation in which every tray represents a separate point of vapour-liquid equilibrium, the vapour-liquid equilibrium curve in a packed column is continuous. However, when modeling packed columns, it is useful to compute a number of theoretical stages to denote the separation efficiency of the packed column with respect to more traditional trays. Differently shaped packings have different surface areas and void space between packings. Both of these factors affect packing performance.

Another factor in addition to the packing shape and surface area that affects the performance of random or structured packing is the liquid and vapour distribution entering the packed bed. The number of theoretical stages required for a given separation is calculated using a specific vapour to liquid ratio. If the liquid and vapour are not evenly distributed across the superficial tower area as it enters the packed bed, the liquid to vapour ratio will not be correct in the packed bed and the required separation will not be achieved. The packing will appear not to be working properly. The height equivalent of a theoretical plate (HETP) will be greater than expected. The problem is not the packing itself but the mal-distribution of the fluids entering the packed bed. Liquid mal-distribution is more frequently the problem than vapour. The design of the liquid distributors used to introduce the feed and reflux to a packed bed is critical to making the packing perform to its maximum efficiency. Methods of evaluating the effectiveness of a liquid distributor to evenly distribute the liquid entering a packed bed can be found in references. Considerable work has been done on this topic by Fractionation Research, Inc. (commonly known as FRI).

Multi-Effect Distillation

The goal of multi-effect distillation is to increase the energy efficiency of the process, for use in desalination, or in some cases one stage in the production of ultrapure water. The number of effects is proportional to the $\text{Kw}\cdot\text{h}/\text{m}^3$ of water recovered figure, and refers to the volume of water recovered per unit of energy compared with single-effect distillation. One effect is roughly $636 \text{ Kw}\cdot\text{h}/\text{m}^3$.

- Multi-stage flash distillation can achieve more than 20 effects with thermal energy input.

- Vapour compression evaporation. Commercial large-scale units can achieve around 72 effects with electrical energy input, according to manufacturers.

There are many other types of multi-effect distillation processes, including one referred to as simply multi-effect distillation (MED), in which multiple chambers with intervening heat exchangers are employed.

3.2.3 Reactors

Chemical reactors are vessels designed to contain chemical reactions. The design of a chemical reactor deals with multiple aspects of chemical engineering. Chemical engineers design reactors to maximise net present value for the given reaction. Designers ensure that the reaction proceeds with the highest efficiency towards the desired output product, producing the highest yield of product while requiring the least amount of money to purchase and operate. Normal operating expenses include energy input, energy removal, raw material costs, labour, etc. Energy changes can come in the form of heating or cooling, pumping to increase pressure, frictional pressure loss (such as pressure drop across a 90° elbow or an orifice plate), agitation, etc.

Both types can be used as continuous reactors or batch reactors. Most commonly, reactors are run at steady-state, but can also be operated in a transient state. When a reactor is first brought back into operation (after maintenance or in operation) it would be considered to be in a transient state, where key process variables change with time. Both types of reactors may also accommodate one or more solids (reagents, catalyst, or inert materials), but the reagents and products are typically liquids and gases.

There are three main basic models used to estimate the most important process variables of different chemical reactors:

- batch reactor model (batch)
- continuous stirred-tank reactor model (CSTR)
- plug flow reactor model (PFR).

Furthermore, catalytic reactors require separate treatment, whether they are batch, CST, or PF reactors, as the many assumptions of the simpler models are not valid.

Key process variables include:

- residence time (τ , lower case Greek tau)
- volume (V)
- temperature (T)
- pressure (P)
- concentrations of chemical species ($C_1, C_2, C_3, \dots C_n$)
- heat transfer coefficients (h, U).

A chemical reactor, typically tubular reactor, could be a packed bed such as multi-bed reactor, multi-tube reactor and tubular high pressure reactor. The packing inside the bed may have catalyst to catalyse the chemical reaction. A chemical reactor may also be a fluidised bed.

Chemical reactions occurring in a reactor may be exothermic, meaning giving off heat, or endothermic, meaning absorbing heat. A chemical reactor vessel may have a cooling or heating jacket or cooling or heating coils (tubes) wrapped around the outside of its vessel wall to cool down or heat up the contents.

3.2.4 Types of Reactor

a) Continuous Stirred-Tank Reactors (CSTRs) and Fluidised Bed Reactors (FBs)

A continuous stirred-tank reactor is an idealised reactor in which the reactants are dumped in one large tank, allowed to react, and then the products (and unused reactants) are released out of the bottom. In this way the reactants are kept relatively dilute, so the temperatures in the reactor are generally lower. This also can have advantages or disadvantages for the selectivity of the reaction, depending on whether the desired reaction is faster or slower than the undesired one. The schematic descriptions of both the continuous stirred-tank (CSTR) and fluidised bed (FB) reactors are illustrated in Fig. 3.

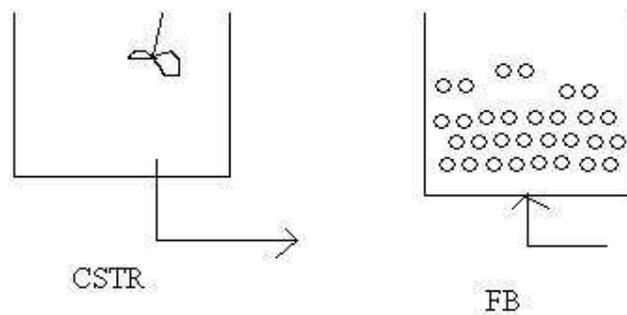


Fig.3: Schematic descriptions of Continuous Stirred-Tank Reactors (CSTRs) and Fluidised Bed Reactors (FBs)

CSTRs are generally more useful for liquid-phase reactions than PFRs since less transport power is required. However, gas-phase reactions are harder to control in a CSTR.

In a CSTR, one or more fluid reagents are introduced into a tank reactor equipped with an impeller while the reactor effluent is removed. The impeller stirs the reagents to ensure proper mixing. By simply dividing the volume of the tank by the average volumetric flow rate through the tank gives the residence time, or the average amount of time a discrete quantity of reagent spends inside the tank. Using chemical kinetics, the reaction's expected percent completion can be calculated. Some important aspects of the CSTR are:

- i. At steady-state, the in-flow rate must equal the mass out-flow rate, otherwise the tank will overflow or go empty (transient state). While the reactor is in a transient state the model equation must be derived from the differential mass and energy balances.
- ii. The reaction proceeds at the reaction rate associated with the final (output) concentration.
- iii. Often, it is economically beneficial to operate several CSTRs in series. This allows, for example, the first CSTR to operate at a higher reagent concentration and therefore a higher reaction rate. In these cases, the sizes of the reactors may be varied in order to minimise the total capital investment required to implement the process.
- iv. It can be seen that an infinite number of infinitely small CSTRs operating in series would be equivalent to a PFR.

The behaviour of a CSTR is often approximated or modeled by that of a Continuous Ideally Stirred-Tank Reactor (CISTR). All calculations

performed with CISTRs assume perfect mixing. If the residence time is 5-10 times the mixing time, this approximation is valid for engineering purposes. The CISTR model is often used to simplify engineering calculations and can be used to describe research reactors. In practice it can only be approached, particularly in industrial size reactors.

A fluidised bed reactor is, in essence, a CSTR which has been packed with catalyst. The same analogy holds between an FB and CSTR as does between a PFR and a PBR. Unlike CSTRs though, fluidised beds are commonly used with gasses; the gas is pumped in the bottom and bubbles through the catalyst on the way to the top outlet.

b) Plug Flow Reactors (PFRs) and Packed Bed Reactors (PBRs)

A plug flow reactor is a (idealised) reactor in which the reacting fluid flows through a tube at a rapid pace, but without the formation of eddies characteristic of rapid flow. Plug flow reactors tend to be relatively easy to construct (they are essentially pipes) but are problematic in reactions which work better when reactants (or products) are dilute.

Plug flow reactors can be combined with membrane separators in order to increase the yield of a reactor. The schematic diagram is shown in Fig.4. The products are selectively pulled out of the reactor as they are made so that the equilibrium in the reactor itself continues to shift towards making more products.

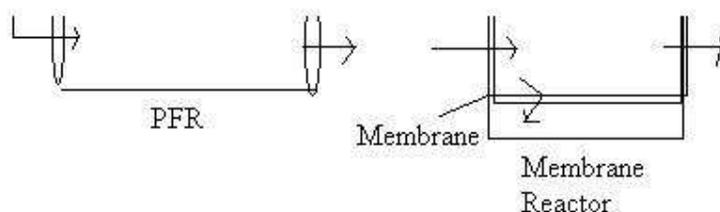


Fig.4: Schematic Diagram of Plug Flow and Membrane Reactors

In a PFR, one or more fluid reagents are pumped through a pipe or tube. The chemical reaction proceeds as the reagents travel through the PFR. In this type of reactor, the changing reaction rate creates a gradient with respect to distance traversed; at the inlet to the PFR the rate is very high, but as the concentrations of the reagents decrease and the concentration of the product(s) increases the reaction rate slows down. An important feature of PFR is that a packed bed reactor is essentially a plug flow reactor packed with catalyst beads. They are used if, like the majority of reactions in industry, the reaction requires a catalyst to significantly progress at a reasonable temperature.

Bioreactors

A bioreactor is a reactor that utilises either a living organism or one or more enzymes from a living organism to accomplish a certain chemical transformation. Bioreactors can be either CSTRs (in which case they are known as **Chemostats**) or PFRs.

Certain characteristics of a bioreactor must be more tightly controlled than they must be in a normal CSTR or PFR because cellular enzymes are very complex and have relatively narrow ranges of optimum activity. These include, but are not limited to:

1. Choice of organism. This is similar to the choice of catalyst for an inorganic reaction.
2. Strain of the organism. Unlike normal catalysts, organisms are very highly manipulable to produce more of what you are after and less of other products. However, also unlike normal catalysts, they generally require a lot of work to get any significant production at all.
3. Choice of substrate. Many organisms can utilise many different carbon sources, for example, but may only produce what you want from one of them.
4. Concentration of substrate and aeration. Two inhibitory effects exist which could prevent you from getting the product you are after. Too much substrate leads to the **glucose effect** in which an organism will ferment regardless of the air supply, while too much air will lead to **Pasteur Effect** and a lack of fermentation.
5. pH and temperature: Bacterial enzymes tend to have a narrow range of optimal pH and temperatures, so these must be carefully controlled.

However, bioreactors have several distinct advantages. One of them is that enzymes tend to be stereo-specific. For example, you don't get useless D-sorbose in the production of vitamin C, but you get L-sorbose, which is the active form. In addition, very high production capacities are possible after enough mutations have been induced. Finally, substances which have not been made artificially or which would be very difficult to make artificially (like most antibiotics) can be made relatively easily by a living organism.

All calculations performed with PFRs assume no upstream or downstream mixing, as implied by the term "plug flow".

Reagents may be introduced into the PFR at locations in the reactor other than the inlet. In this way, a higher efficiency may be obtained, or the size and cost of the PFR may be reduced.

A PFR typically has a higher efficiency than a CSTR of the same volume. That is, given the same space-time, a reaction will proceed to a higher percentage completion in a PFR than in a CSTR.

For most chemical reactions, it is impossible for the reaction to proceed to 100% completion. The rate of reaction decreases as the percent completion increases until the point where the system reaches dynamic equilibrium (no net reaction, or change in chemical species occurs). The equilibrium point for most systems is less than 100% complete. For this reason a separation process, such as distillation, often follows a chemical reactor in order to separate any remaining reagents or byproducts from the desired product. These reagents may sometimes be reused at the beginning of the process, such as in the Haber process.

c) Continuous Oscillatory Baffled Reactor (COBR)

It is a tubular plug flow reactor. The mixing in COBR is achieved by the combination of fluid oscillation and orifice baffles, allowing plug flow to be achieved under laminar flow conditions with the net flow Reynolds number just about 100.

d) Semi-Batch Reactor

A semi-batch reactor is operated with both continuous and batch inputs and outputs. A fermenter, for example, is loaded with a batch, which constantly produces carbon dioxide, and has to be removed continuously. Analogously, driving a reaction of gas with a liquid is usually difficult, since the gas bubbles off. Therefore, a continuous feed of gas is injected into the batch of a liquid. One chemical reactant is charged to the vessel and a second chemical is added slowly.

e) Catalytic Reactor

Although catalytic reactors are often implemented as plug flow reactors, their analysis requires more complicated treatment. The rate of a catalytic reaction is proportional to the amount of catalyst the reagents contact. With a solid phase catalyst and fluid phase reagents, this is proportional to the exposed area, efficiency of diffusion of reagents in and products out, and turbulent mixing or lack thereof. Perfect mixing cannot be assumed. Furthermore, a catalytic reaction pathway is often multi-step with intermediates that are chemically bound to the catalyst; and as the chemical binding to the catalyst is also a chemical reaction, it may affect the kinetics.

The behaviour of the catalyst is also a consideration. Particularly in high-temperature petrochemical processes, catalysts are deactivated by sintering, coking, and similar processes.

3.2.5 Separators

The term separator in oil field terminology designates a pressure vessel used for separating well fluids produced from oil and gas wells into gaseous and liquid components. A separator for petroleum production is a large vessel designed to separate production fluids into their constituent components of oil, gas and water. A separating vessel may be referred to in the following ways: oil and gas separator, separator, stage separator, trap, knockout vessel (knockout drum, knockout trap, water knockout, or liquid knockout), flash chamber (flash vessel or flash trap), expansion separator or expansion vessel, scrubber (gas scrubber), filter (gas filter). These separating vessels are normally used on a producing lease or platform near the wellhead, manifold, or tank battery to separate fluids produced from oil and gas wells into oil and gas or liquid and gas. An oil and gas separator generally includes the following essential components and features:

1. A vessel that includes (a) primary separation device and/or section, (b) secondary “gravity” settling (separating) section, (c) mist extractor to remove small liquid particles from the gas, (d) gas outlet, (e) liquid settling (separating) section to remove gas or vapor from oil (on a three-phase unit, this section also separates water from oil), (f) oil outlet, and (g) water outlet (three-phase unit).
2. Adequate volumetric liquid capacity to handle liquid surges (slugs) from the wells and/or flow lines.
3. Adequate vessel diameter and height or length to allow most of the liquid to separate from the gas so that the mist extractor will not be flooded.
4. A means of controlling an oil level in the separator, which usually includes a liquid-level controller and a diaphragm motor valve on the gas outlet.
5. A back pressure valve on the gas outlet to maintain a steady pressure in the vessel.
6. Pressure relief devices.

Separators work on the principle that the three components have different densities, which allows them to stratify when moving slowly with gas on top, water on the bottom and oil in the middle. Any solids such as sand will also settle in the bottom of the separator.

Other examples of separators are centrifuge, hydrocyclone, liquid- liquid separators, gas- liquid separators.

3.2.6 Mixers

The several available mixers that are normally used for the continuous mixing of low viscosity fluids include inline mixer such as simple mixing tee, and injection mixers. They are static devices which promote turbulent mixing in pipelines.

In static mixer, materials flowing are mixed solely by redirecting fluid flow to follow the geometry. The only power required for static mixers is the external pumping power that propels the material through the mixer. Static mixers employ the principle of dividing the flow and recombining it in a geometric sequence. It is also called a **Motionless Mixer**.

Other types of mixers are stirred tanks which are mixing vessels fitted with some form of agitator for blending liquids and preparing solutions.

The overall system design is dependent on many variables including the physical properties of fluids, mixer length, tube inner diameter, the number of elements and their geometrical design.

3.2.7 Crushers

A crusher is a machine designed to reduce large rocks into smaller rocks, gravel, or rock dust. Crushers may be used to reduce the size, or change the form, of waste materials so they can be more easily disposed of or recycled, or to reduce the size of a solid mix of raw materials (as in rock ore), so that pieces of different composition can be differentiated. Crushing is the process of transferring a force amplified by mechanical advantage through a material made of molecules that bond together more strongly, and resist deformation more, than those in the material being crushed. Crushing devices hold material between two parallel or tangent solid surfaces, and apply sufficient force to bring the surfaces together to generate enough energy within the material being crushed so that its molecules separate from (fracturing), or change alignment in relation to (deformation), each other. The earliest crushers were hand-held stones, where the weight of the stone provided a boost to muscle power, used against a stone anvil. Querns and mortars are types of these crushing devices.

In industry, crushers are machines which use a metal surface to break or compress materials. Mining operations use crushers, commonly classified by the degree to which they fragment the starting material,

with primary and secondary crushers handling coarse materials, and tertiary and quaternary crushers reducing ore particles to finer gradations. Each crusher is designed to work with a certain maximum size of raw material, and often delivers its output to a screening machine which sorts and directs the product for further processing. Typically, crushing stages are followed by milling stages if the materials need to be further reduced. Additionally rock-breakers are typically located next to a crusher to reduce oversize material too large for a crusher. Crushers are used to reduce particle size enough so that the material can be processed into finer particles in a grinder.

In operation, the raw material (of various sizes) is usually delivered to the primary crusher's hopper by dump trucks, excavators or wheeled front-end loaders. A feeder device such as an apron feeder, conveyor or vibrating grid controls the rate at which this material enters the crusher, and often contains a preliminary screening device which allows smaller material to bypass the crusher itself, thus improving efficiency. Primary crushing reduces the large pieces to a size which can be handled by the downstream machinery.

4.0 CONCLUSION

Heat exchangers, distillers, reactors, separators are among the very many chemical technology equipment available for industrial processes. Others are grinder, crusher, autoclave, hydrocyclone, stirred tank, compressor, furnace, ejector and column such as tray and packed columns. All the equipment helps to facilitate production in the industry.

5.0 SUMMARY

You have learnt in this unit that the raw materials are treated through physical steps (unit operation) to make it suitable for chemical reaction (unit process) and this involved the use of different types of equipment for the objectives to be realised. Consequently, typical equipment such as heat exchanger, distillation column, reactors and separators that are commonly found in the industries were discussed. Others such as crushers, grinders, mixers are also commonly used.

6.0 TUTOR- MARKED ASSIGNMENT

- i. What are heat exchangers?
- ii. List some examples of heat exchangers.
- iii. State the different types of reactor.
- iv. Explain briefly the importance of a reactor.
- v. With respect to named equipment, discuss the use of equipment in the industry.

7.0 REFERENCES/FURTHER READING

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